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The attached documents are exact copies of the European patent application described on the following page, as originally filed.

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Patentanmeldung Nr. Patent application No. Demande de brevet n°

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For the President of the European Patent Office

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SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.
2596 HR Den Haag
NETHERLANDS

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PROCESS FOR THE CARBOXYLATION OF CONJUGATED DIENES

The present invention relates to a process for the carbonylation of conjugated dienes, whereby a conjugated diene is reacted with carbon monoxide and a hydroxyl group containing compound in the presence of a catalyst system including a source of palladium cations, a phosphorus-containing ligand and a source of anions. In particular it relates to the preparation of alkyl pentenoates and/or adipates from 1,3-butadiene and derivatives thereof.

US Patent Specification No. 5,495,041 discloses a process for the preparation of a pentenoate ester by carbonylation of butadiene or a butadiene derivative in the presence of carbon monoxide, alcohol and a catalyst system comprising palladium, a carboxylic acid and a phosphine ligand, wherein the carboxylic acid is pentenoic acid. Preferably a monodentate phosphine ligand is used to obtain a high selectivity. The molar ratio of butadiene or a butadiene derivative to palladium in this case is less than 70:1, preferably less than 20:1.

European patent No. 0198521 discloses a process for preparing carboxylic di-esters or dicarboxylic acids by the reaction of a conjugated diene with carbon monoxide and an alkanol or water in the presence of an aprotic solvent and a dissolved catalyst system comprising a divalent palladium compound, a triaryl phosphine and hydrogen chloride. The catalyst system may further comprise a bidentate phosphine. In its examples it is illustrated that the process can also be used for the preparation of mono-esters.

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The conversion of 1,3-butadiene to carboxylic diesters or to mono-esters is performed in one step. However, at least one mole of hydrogen chloride per atom of trivalent phosphorus present in the catalytic system
5 is considered necessary, as a result of which supplementary, cost-increasing measures are required to avoid corrosion. Examples disclose that the molar ratio of conjugated diene to palladium is about 115:1.

Object of the present invention, is to provide an
10 improved process for carbonylation of conjugated dienes.

An improved process has now, surprisingly, been found for the selective conversion of conjugated dienes such as 1,3-butadiene, with a high conversion rate, in the presence of a specific catalyst system. This specific
15 catalyst system has an unexpectedly high activity, which allows for molar ratios well over 200:1 and suitably well over 300:1 of conjugated diene to palladium to be used, while obtaining high selectivities. Thus, the amount of catalyst to be consumed in the process can be reduced
20 whereby the cost of the process will be reduced. Further advantages are that high conversion rates are achieved without the necessity of halides, thus allowing cheaper types of steel for the reactor installations.

The process is specifically directed to the
25 carbonylation of conjugated dienes, which show specific reaction characteristics when compared to olefins in general. Conjugated dienes contain at least two conjugated double bonds in the molecule. By conjugation is meant that the location of the π -orbital is such that it can overlap other orbitals in the molecule. Thus, the effects of compounds with at least two conjugated double bonds are often different in several ways from those of compounds with no conjugated bonds. It is generally
30 acknowledged that the carbonylation of conjugated dienes comprises more difficulties than that of a mono-olefin.
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For example, in European patent No. EP 0495548, regarding the carbonylation of olefins, it is stated that diolefins with more than one unsaturated double bond may be used, however, in particular those wherein the double bonds are non-conjugated.

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The present invention therefore provides a process for the carbonylation of conjugated dienes, whereby a conjugated diene is reacted with carbon monoxide and a hydroxyl group containing compound in the presence of a catalyst system based on:

- (a) a source of palladium cations,
- (b) a phosphorus-containing ligand
- (c) a source of anions,

wherein the phosphorus-containing ligand is a ligand having the general formula I



wherein X^1 and X^2 represent a substituted or non-substituted cyclic group with at least 5 ring atoms, of which one is a phosphorus atom, and R represents a bivalent organic bridging group, connecting both phosphorus atoms, containing from 1 to 4 atoms in the bridge.

Carbonylation includes mono- and di-carbonylation.

The process can be used to prepare both mono-esters and/or diesters in one step. Mono-esters can be formed in high selectivity. By varying reaction conditions such as the residence time, the pressure, the temperature, the amount of hydroxyl group containing compound, the source of anions and specific type of ligand, the process can be made more selective to either mono-esters or diesters as will be described in more detail below.

The conjugated diene preferably is a conjugated diene having from 4 to 20, more preferably from 4 to 8 carbon atoms per molecule. Preferably, the conjugated diene is

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1,3-butadiene or a derivative thereof, wherein the butadiene is substituted, suitably with an alkyl, alkoxy, carbonyl or aldehyde group or a sulphur, nitrogen, phosphor or halide containing group. Most preferably the conjugated diene is 1,3-butadiene.

Preferred hydroxyl group containing compounds in the process of the invention are alkanols with 1 to 20, more preferably with 1 to 6 carbon atoms per molecule and alkanediols with 2-20, more preferably 2 to 6 carbon atoms per molecule. Suitable alkanols in the process of the invention include methanol, ethanol, propanol, i-propanol, butanol, s-butanol, t-butanol, pentanol, hexanol, cyclohexanol and phenol. Preferably methanol or ethanol is used as a hydroxyl group containing compound.

The use of these alkanols or alkanediols as a hydroxyl group containing compound in the carboxylation process of 1,3-butadiene and derivatives thereof enables the production of alkyl pentenoates and alkyl adipates and derivatives thereof of which the alkyl group contains 1 to 20, more preferably 1 to 6, carbon atoms.

Methanol is especially preferred as a hydroxyl group containing compound. The use of methanol as a hydroxyl group containing compound in the carboxylation process of 1,3-butadiene enables the production of methyl-pentenoate and/or dimethyl adipate. Methyl-pentenoate is an important intermediate in the production process of caprolactam. For the preparation of caprolactam, methyl-pentenoate is hydroformylated to methyl formylvalerate, which after reductive amination and cyclisation forms caprolactam. Caprolactam is a starting materials in the manufacture of fibres or engineering plastics. Hydroformylation, reductive amination and cyclisation can be performed in any manner known to a person skilled in the art. Suitable processes are given in PCT application

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No. WO 95/0625 and Japanese patent application
No. JP-A-25351/66.

The skilled reader will further realise that the process of the present invention can also be used to 5 prepare carboxylic mono-acids and/or carboxylic diacids.

Carboxylic mono-acids and/or carboxylic diacids are prepared by reacting conjugated dienes with carbon monoxide and using water as a hydroxyl group containing compound. In this case, the carbonylation product, i.e. 10 the carboxylic acid or di-acid can be used as the source of anions.

A suitable source for palladium cations of component (a) are its salts. Suitable salts include salts of halide acids, such as palladium (II) chloride or palladium(II)- 15 bromide palladium (II) Iodide, of mineral acids, such as palladium(II)sulphate, palladium(II)nitrate and palladium(II)phosphate, and organic salts, such as acetylacetones and salts of sulphonic acids.

Preferably, a salt of a carboxylic acid is used, 20 suitably a carboxylic acid with up to 10 carbon atoms, such as salts of acetic acid, propionic acid and butanoic acid, or salts of substituted carboxylic acids such as trichloroacetic acid and trifluoroacetic acid. A very suitable source is palladium(II) acetate.

25 The phosphorus-containing ligand of component (b) of the general formula I



represents a bidentate ligand wherein x^1 and x^2 represent 30 a substituted or non-substituted cyclic group with at least 5 ring atoms, of which one is a phosphorus atom, and R represents a bivalent organic bridging group, connecting both phosphorus atoms, containing from 1 to 4 atoms in the bridge.

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By "a bridge" is understood the shortest connection between both phosphorus atoms. Preferably, the bridging group R represents an alkylene group containing from 1 to 4 carbons atoms in the bridge, but it may also comprise a carbon chain, interrupted by a hetero atom, such as nitrogen, sulphur, silicon or oxygen atom. The alkylene group can be substituted or non-substituted or can form part of a aliphatic or aromatic ring structure. Most preferably, R represents a substituted or non-substituted ethylene or propylene group, connecting both phosphorus atoms by the first and the second or the third carbon atom, such as a 1,2-ethylene, a 1,2-propylene or a 1,3-propylene group.

x¹ and x² represent a substituted or non-substituted cyclic group with at least 5 ring atoms, of which one is a phosphorus atom, and preferably with from 6 to 10 ring atoms. More preferably x¹ and x² represent a substituted or non-substituted cyclic group with 9 ring atoms, of which one is a phosphorus atom. By "a cyclic group" is understood a monocyclic or polycyclic group. Preferred cyclic groups are bicyclic groups. Particularly preferred is a substituted or non-substituted bicyclononyl group wherein one carbon atom is replaced by the phosphorus atom, i.e. a 9-phosphabicyclononyl group. The 9-phosphabicyclononyl group can have several isomeric structures. For the purpose of the invention the [3,3,1] and [4,2,1] isomers are preferred. Suitably x¹ and x² are substituted or non-substituted [3,3,1] or [4,2,1] 9-phosphabicyclononyl groups. The two 9-phosphabicyclononyl groups can have both the same or each a different isomeric structure.

One or both of the phosphabicyclononyl rings can be substituted with one or more suitable hydrocarbyl groups containing carbon atoms and/or hetero atoms. Suitable

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substituents include groups containing hetero-atoms such as halides, sulphur, phosphor, oxygen and nitrogen.

Examples of such groups include chloride, bromide, iodide, thiol, and groups of the general formula R^2-O- , $-S-R^2$, $-CO-R^2$, $-NH_2$, $-NHR^2$, $-NR^2R^3$, $-CO-NR^2R^3$, $-OH$, $-PO_4$,

5 $-NO_2$, $-NOH$, $-CO$, $-SO_2$, $-SOH$, in which R^2 and R^3 , independently, represent hydrocarbyl groups like methyl, ethyl, propyl and isopropyl. Groups containing carbon-

10 atoms include straight-chain or branched saturated or non-saturated carbon containing groups. If a phosphabi-cyclononyl ring is substituted it is preferably substituted with a carbon containing group. Such a carbon containing group can, however, contain additional hetero atoms, such as halides, sulphur, oxygen and nitrogen or

15 hetero-groups as described hereinbefore. Preferably, substituted phosphabicyclononyl rings are substituted with alkyl groups, preferably having from 1 to 10 carbon atoms, more preferably from 1 to 4 carbon atoms. Linear, branched or cyclic alkyl groups can be used. Suitable

20 alkyl groups include, methyl, ethyl, propyl, iso-propyl, butyl and iso-butyl. More suitably methyl groups are used. The substituted phosphabicyclononyl ring can be mono- or poly-substituted and is preferably di-substituted. Most preferably the phosphabicyclononyl ring is

25 substituted with two methyl groups. The phosphabicyclo-nonyl ring can be substituted at all carbon atoms of the ring. However, the use of rings with substitutents on certain carbon atoms can be more beneficial. Suitably, rings are used with substituents on two carbon atoms,

30 suitably carbon atom 1, 2, 8 and carbon atom 4, 5 or 6.

Suitable phosphorus-containing ligands of formula (I) thus include substituted or non-substituted: symmetric or asymmetric [3,3,1] or [4,2,1] isomers of 1,3-P,P'-bis(9-phosphabicyclononyl)propane;

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symmetric or asymmetric [3,3,1] or [4,2,1] isomers of 1,2-P,P'bis(9-phosphabicyclononyl)propane; symmetric or asymmetric [3,3,1] or [4,2,1] isomer of 1,2-P,P'bis(9-phosphabicyclononyl)ethane; and mixtures of above mentioned compounds.

5 The selectivity of the process to either mono-esters or diesters can be partly regulated by the phosphorus-containing ligand used. Diesters are most suitably prepared with a catalyst system wherein the phosphorus-10 containing ligands of formula (I) are non-substituted.

For the preparation of mono-esters one or both of the phosphabicyclononyl rings of the abovementioned phosphorus-containing ligands is preferably substituted. Suitable substituted diphosphines for the preparation of 15 mono-esters include, symmetric or asymmetric [3,3,1] or [4,2,1] isomers of 1,2-P,P' bis(1,5-dimethyl, 9-phosphabicyclononyl)ethane and mixtures thereof or symmetric or asymmetric [3,3,1] or [4,2,1] isomers of 1,3-P,P' bis-(1,5-dimethyl, 9-phosphabicyclononyl)propane and mixtures thereof or symmetric or asymmetric [3,3,1] or [4,2,1] 20 isomers of 1,2-P,P' bis (1,5-dimethyl 9-phosphabicyclononyl)propane and mixtures thereof, or a combination of above mentioned diphosphines.

The invention therefore further provides a catalyst 25 system based on:

- (a) a source of palladium cations,
 - (b) a phosphorus-containing ligand
 - (c) a source of anions,
- wherein the phosphorus-containing ligand is a ligand 30 having the general formula I



wherein X^1 and X^2 represent a substituted cyclic group with at least 5 ring atoms, of which one is a phosphorus atom, and R represents a bivalent organic bridging group,

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connecting both phosphorus atoms, containing from 1 to 4 atoms in the bridge.

Preferred embodiments are the same as those described for the process hereinbefore. Suitably one or both cyclic groups X¹ and X² are substituted with one or more hydrocarbyl groups containing carbon atoms and/or hetero atoms, preferably with carbon containing groups. More preferably one or both cyclic groups X¹ and X² are substituted with one or more alkyl groups having from 1 to 4 carbon atoms. Suitably the substituted cyclic group is a substituted bicyclic group, more suitably a substituted [3,3,1] or [4,2,1] 9-phosphabicyclononyl group. This substituted [3,3,1] or [4,2,1] 9-phosphabicyclononyl group is preferably substituted with two alkyl groups, preferably methyl groups, on carbon atom 1, 2 or 8 and carbon atom 4, 5 or 6.

The above mentioned phosphorus-containing ligands can be prepared by refluxing the phosphabicyclononane hydride with 1,2-dibromoethane in acetonitrile. After neutralisation with sodium hydroxide the bis (9-phosphabicyclononyl)ethane can be isolated. The phosphabicyclononane hydride may conveniently be prepared as described by Elsner et al. (Chem. Abstr. 1978, vol. 89, 180154x). Substituted phosphabicyclononane hydride is conveniently prepared by using substituted cyclooctadienes in the hereinbefore mentioned process described by Elsner et al.

Surprisingly the use of the above mentioned substituted and / or non-substituted phosphorus-containing ligands renders the catalyst system much more active. The prior art teaches away from the ligands presently used. In US Patent Specification No. 5,495,041, for example, a wide range of phosphorus-containing ligands is mentioned. However, in its examples it teaches

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the preferred use of monodentate or bidentate phenyl substituted phosphines. In European patent No. 0198521 also monodentate or bidentate phosphines are preferably substituted with phenyl groups, as is illustrated in its examples. The aryl phosphines preferred in this prior art have characteristics completely different from those of the cyclic phosphine ligands specified above for the present catalyst system. The present catalyst system, however, has an unexpectedly high activity, which allows for high molar ratios well above 200:1 and suitably well over 300:1 of conjugated diene to palladium to be used, while still obtaining high selectivities. The high activity of the catalyst system of this invention allows the amount of catalyst system to be reduced by more than 40% as compared to the amount of catalyst system used in the prior art.

The source of anions of component (c) can essentially be any salt or acid or a combination of salt and acid.

Preferably an acid is used. A wide range of acids can be used, including halide acids, such as hydrochloric acid and hydrobromic acid, mineral acids, such as sulphuric acid, nitric acid and phosphoric acid, and organic acids, such as acetylacetonic acids, sulphonic acids and carboxylic acids. Preferably, a protonic acid is used, such as sulphuric acid, phosphoric acid and carboxylic acids. More preferably a carboxylic acid is used.

When a protonic acid, preferably a carboxylic acid, is used, preferably an acid with a pKa value > 1 in aqueous solution at a temperature of 25 °C is used.

Suitable salts include any salts formed with inert substantially non-coordinating cations, such as sodium or potassium. Suitable salts includ salts of halide acids, such as chloride salts and bromide salts, of mineral acids, such as sulphate salts, carbonate salts and

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phosphate salts, and organic salts, such as acetyl-acetonates, salts of sulphonic acids and carboxylic acids. Preferably carboxylate salts are used and more preferably carboxylate salts are used of which the corresponding carboxylic acid has a pKa value > 1 in aqueous solution at a temperature of 25 °C.

In a possible embodiment the source of anions is the same as the source of palladium cations in using a palladium salt. Preferred palladium salts are the palladium carboxylate salts.

The selectivity of the process to either mono-esters or diesters can be partly regulated by the source of anions used. Suitable anions for the preparation of diesters, include benzoic acid or benzoic salts or a derivative thereof. The benzoic acid or salt can be substituted. Suitable substituents include halide groups, hydrocarbyl groups, carboxy groups and alkoxy groups. Especially suitable anions for the preparation of diesters include benzoic acids or salts substituted with methoxy groups, such as 2,6-dimethoxybenzoic acid and salts thereof.

For the preparation of mono-esters, as a source of anions preferably the carboxylic acid is used, which results from the carbonylation reaction of the conjugated diene with carbon monoxide and water or obtainable by hydrolysis of the ester product, thus the acid derivative of the ester product to be prepared. For example, if the conjugated diene is 1,3-butadiene, component (c) might conveniently be pentenoic acid, pentenoic acid being the product of the carbonylation of 1,3-butadiene with carbon monoxide and water. Component (c) of the catalyst system might thus be different for each conjugated diene used. The advantage is that any reaction of the component (c) with the hydroxyl group containing compound results in the same product as obtained by the carbonylation of the

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conjugated diene with that hydroxyl group containing compound.

The source of anions can furthermore be any combination of hereinbefore mentioned acids and salts.

5 The molar ratio of acid and salt can vary between wide limits and suitably lies in the range of 100:1 to 1:100, more suitably in the range of 100:1 to 1:1. In a suitable embodiment for the preparation of diesters, an carboxylic acid is combined with an under the reaction conditions
10 substantially less-coordinating salt.

The selectivity of the process to either mono-esters or diesters can further be regulated by means of residence time. Residence time in the reaction vessel can vary with other factors such as the specific ligand used,
15 the source of anions used and the pressure. Optimal residence times in the reaction vessel might further be determined dependent of other factors known to one skilled in the art such as the catalyst concentration used and the size of the reaction vessel. Residence time
20 can be very short, even in the range of seconds, dependent of a continuous, semi-continuous or batch-wise process is being used. For a batch-wise process, suitably the residence times are in the range to 48 hours, more suitably in the range of 10 minutes to 15 hours.
25 Generally a residence time near the upper limit of this range favours the preparation of diesters and a residence time near the lower limit of this range favours the preparation of mono-esters.

The selectivity of the process to either mono-esters or diesters can also be influenced by means of pressure. Reaction pressures may be atmospheric or superatmospheric. In particular the pressures are conveniently ranging from 1 to 100 bar, preferably 1-30 bar.

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The use of a low pressure favours the preparation of diesters, while the use of a higher pressure favours the preparation of mono-esters. The pressure used for a specific set of reactants and required product may be determined by simple experimentation. The ratio of mono-esters and diesters prepared at a certain pressure can further be regulated by other reaction conditions as mentioned herein.

Carbon monoxide partial pressures in the range of 1-65 bar are preferred. In the process according to the present invention, the carbon monoxide can be used in its pure form or diluted with an inert gas such as nitrogen, carbon dioxide or noble gases such as argon.

The molar ratio of conjugated dienes, in particular butadiene, and hydroxyl group containing compound can vary between wide limits and suitably lies in the range of 1:0.1 to 1:10, more suitably from 1:1 to 1:6. Generally a molar ratio near the lower limit of this range favours the preparation of diesters and a molar ratio near the higher limit of this range favours the preparation of mono-esters. The amount of hydroxyl group containing compound to be used for the preparation of mono-esters and/or di-esters needs to be optimised in relation to other hereinbefore described factors that influence the ratio between mono-esters and diesters prepared, such as residence time and pressure.

The selectivity of the process to a certain compound, expressed in a percentage, is defined as:

$$\frac{a}{b} \times 100\%$$

wherein "a" is the amount of conjugated diene that has been converted into that certain compound and "b" the total amount of converted conjugated diene.

It will be clear that a very high selectivity for the conversion of the conjugated diene in the mono-ester or

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derivatives thereof is obtained at the cost of the conversion in the diester or derivatives thereof.

The carbonylation process can be performed batchwise, semi-continuously or continuously. Preferably a

5 continuous manner of operation is used. The continuous process is preferably carried out in a stripping reactor, although it may also be conducted as a continuous process as disclosed in European patent application

10 No. EP-A-0,279,477. In the process of the invention the stripping reactor concept comprises reacting an hydroxyl group containing compound in a liquid phase with a conjugated diene and carbon monoxide in a reaction vessel in the presence of a catalyst system as described hereinbefore, and removing the mono-ester and/or diester

15 reaction product from the reaction vessel in a stream of vapour. The vapour stream may be formed by passing a gas through the reaction vessel. The gas strips the reaction product from the liquid phase in the reaction vessel and so forms a stream of vapour. The gas used to form the

20 stream of vapour may be blown onto the surface of the liquid phase, but is preferably bubbled through it. When gas is bubbled through the liquid phase, it stirs the liquid phase. Any volatile materials present in the liquid phase, other than the reaction product, for

25 example the hydroxyl group containing compound, will also be removed in the stream of vapour. The rate at which gas is passed through the reaction vessel should be sufficient to strip the reaction product from the liquid phase, and may be determined by simple experimentation.

30 Suitably the gas velocity ranges from 5 Nl/hr to 100 Nl/hr. The use of a continuous manner of operation conveniently allows for even higher molar ratios of conjugated diene to palladium and lower residence times to be used.

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The stripping gas used to form the stream of vapour advantageously includes carbon monoxide. It may further comprise conjugated diene, depending on the type of conjugated diene used, and/or other reactants. Although it is possible to use one or more inert gases, for example nitrogen, carbon dioxide and noble gases such as argon, such use is not preferred, because these inert gases eventually have to be separated from the product stream and the reactants. Preferably the gas comprises at least carbon monoxide and preferably also conjugated diene, i.e., the feed. The molar ratio of conjugated diene to carbon monoxide is preferably in the range of from 9:1 to 1:9, more preferably from 2:1 to 1:2. The stream of vapour leaving the reaction vessel may be cooled to afford a gas phase and a liquid phase. The gas phase, including volatile unreacted reactants such as carbon monoxide and, depending on the conjugated diene used, conjugated diene, may be conveniently recycled to the reaction vessel.

The ratio of moles of phosphorus-containing ligand, i.e. catalyst component (b), per mole of palladium cation, i.e. catalyst component (a), ranges from 0.5 to 10, preferably from 1 to 2.

To maintain a constant activity of the catalyst in the continuous process, the source of anions, i.e. catalyst component (c), or water (as a reactant for preparing a source of anions in-situ) are supplied intermittently, or -more preferably- continuously to the reaction vessel to avoid depletion of catalyst component (c) by being stripped from the reaction vessel. The quantity of, for instance in-situ prepared, carboxylic acid used in the carbonylation reaction may vary within wide ranges. Preferably, the amount of acid ranges from 1 mole to 1000 mole of acid per mole of palladium cation.

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The process of the present invention can be used for each range of mole conjugated diene per mole of palladium cation. As described above, conveniently, the amount of catalyst system is small. The ratio of mole conjugated diene per mole of palladium cation can vary between wide limits, suitably in the range from 1×10^1 to 2×10^7 mole conjugated diene per mole of palladium cation, dependent of a continuous, semi-continuous or batch-wise process is being used. The use of a continuous manner of operation conveniently allows for high molar ratios near the upper limit of this range. For a batch-wise process, suitable the ratio of mole conjugated diene per mole of palladium cation is in the range of 2×10^2 to 2×10^6 more suitably in the range of 3×10^2 to 2×10^5

In the process of the invention liquid carbonylation product and/or surplus of a carbonylation reactant such as conjugated diene or hydroxyl group containing compound may serve as solvent during the reaction. It is also possible to perform the reaction in the presence of an extra inert solvent. Suitable extra inert solvents are for example polar, aprotic compounds, such as ketones, ethers (e.g., anisole, tetrahydrofuran or the dimethylether of diethyleneglycol) or sulphones (e.g., sulpholane). Preferably, the liquid carbonylation product and/or the liquid carbonylation reactants serve as a solvent.

The carbonylation reaction is conveniently carried out at moderate temperatures, generally ranging from 20 to 200 °C, preferably ranging from 80 to 180 °C.

The invention will be illustrated by the following non-limiting examples.

Example 1

A 300 ml magnetically stirred autoclave was filled with 40 ml methanol, 40 ml solvent, 0.5 mmol palladium

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acetate, 0.6 mmol 1,2-P,P'-bis(9-phosphabicyclononyl)-ethane (mainly the symmetrical [3,3,1] isomer) and 2 mmol 2,6-dimethoxybenzoic acid. As a solvent anisole was used, which is a non-polar solvent with solvent properties similar to that of esters. Subsequently the autoclave was closed, evacuated and hereafter 20 ml (circa 230 mmol) of 1,3-butadiene was added, thus obtaining a ratio of about 460:1 mole conjugated diene per mole of palladium cation, and carbon monoxide to an initial carbon monoxide pressure of 40 bar was added. The autoclave was heated to 170 °C. After a residence time of 10 hours, the contents of the autoclave were analysed by means of gas-liquid chromatography. The initial rate of carbonylation was 240 mol CO/grams atom palladium/hour. The initial rate of carbonylation was defined as the mean rate of carbon monoxide consumption over the first 30% butadiene conversion. The total selectivity to butadiene carbonylation products was found to be more than 95%. The butadiene carbonylation products consisted of 13% pentenoates and 87% diesters. The diesters consisted of 59% dimethyl-adipate, 19% dimethyl 2-methyl glutarate, 9% dimethyl 2-ethyl succinate glutarate and 13% dimethyl propyl maleate. Traces of vinylcyclohexene and its carbonylation products were formed.

25 Example 2

This experiment was carried out in virtually the same manner as the experiment under example 1, except that instead of 2 mmol 2,6-dimethoxybenzoic acid, 5 mmol 3-pentenoic acid was used as a source of anions. After a residence time of 10 hours, the contents of the autoclave were analysed. The initial rate of carbonylation was 400 mol CO/grams atom palladium/hour. The total selectivity to butadiene carbonylation products was found to be 90%. The butadiene carbonylation products consisted of 57% pentenoates and 43% diesters.

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Comparative Example A

This comparative experiment was carried out in virtually the same manner as the experiment under example 1, except that instead of 0.6 mmol 1,2-P,P'bis-(9-phosphabicyclononyl)ethane, 0.6 mmol 1,2-P,P'bis-(dicyclohexylphosphine)ethane was used as a phosphorus containing ligand. After a residence time of 10 hours, the contents of the autoclave were analysed. The initial rate of carbonylation was only 60 mol CO/grams atom palladium/hour, only a quarter of the initial rate of example 1. The total selectivity to butadiene carbonylation products was found to be less than 60%. The butadiene carbonylation products consisted of 95% pentenoates and 5% diesters.

Example 3

This experiment was carried out in virtually the same manner as the experiment under example 1, except that instead of 2 mmol 2,6-dimethoxybenzoic acid, 5 mmol 2,6-dimethoxybenzoic acid was used as a source of anions. After a residence time of 5 hours, the contents of the autoclave were analysed. The initial rate of carbonylation was 350 mol CO/grams atom palladium/hour. The total selectivity to butadiene carbonylation products was found to be more than 95%. The butadiene carbonylation products consisted of 87% pentenoates and 13% diesters.

Example 4

This experiment was carried out in virtually the same manner as the experiment under example 1. The autoclave was filled with 20 ml methanol, 40 ml anisole, 0.5 mmol palladium acetate, 0.6 mmol 1,2-P,P'bis(1,5-dimethyl, 9-phosphabicyclononyl)ethane (mainly the symmetrical [3,3,1] isomer), 10 mmol 3-pentenoic acid, closed and evacuated. Hereafter 20 ml of 1,3-butadiene and carbon monoxide to an initial carbon monoxide pressure of 40 bar

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was added. The autoclave was heated to 150 °C. After a residence time of 5 hours, the contents of the autoclave were analysed. The initial rate of carbonylation was 300 mol CO/grams atom palladium/hour. The total selectivity to butadiene carbonylation products was found to be more than 95%. The butadiene carbonylation products consisted of 92% pentenoates and 8% diesters.

Example 5

This experiment was carried out in virtually the same manner as the experiment under example 1. The autoclave was filled with 20 ml methanol, 40 ml anisole, 0.5 mmol palladium acetate, 0.6 mmol 1,2-P,P'-bis(9-phosphabicyclononyl)orthoxylene, 10 mmol 2,4,6-trimethylbenzoic acid, closed and evacuated. Hereafter 20 ml of 1,3-butadiene and carbon monoxide to an initial carbon monoxide pressure of 40 bar was added. The autoclave was heated to 150 °C. After a residence time of 5 hours, the contents of the autoclave were analysed. The initial rate of carbonylation was 100 mol CO/grams atom palladium/hour. The total selectivity to butadiene carbonylation products was found to be 95%. The butadiene carbonylation products consisted of 99% pentenoates and 1% diesters.

Comparative Example B

This comparative experiment was carried out in virtually the same manner as the experiment under example 1. The autoclave was filled with 20 ml methanol, 40 ml anisole, 0.5 mmol palladium acetate, 1.0 mmol 1,4-P,P'-bis(diphenylphosphine)butane, 10 mmol 3-pentenoic acid, closed and evacuated. Hereafter 20 ml of 1,3-butadiene and carbon monoxide to an initial carbon monoxide pressure of 40 bar was added. The autoclave was heated to 150 °C. After a residence time of 5 hours, the contents of the autoclave were analysed. The initial rate of carbonylation was only 70 mol CO/grams atom palladium/hour. The total selectivity to butadiene

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carbonylation products was found to 95%. The butadiene carbonylation products consisted of 98% pentenoates and 2% diesters.

Comparative Example C

5 This comparative experiment was carried out in virtually the same manner as the experiment under comparative example B, except that instead of 1.0 mmol 1,4-P,P'bis(diphenylphosphine)butane, 0.6 mmol 1,4-P,P'bis(diphenylphosphine)butane was used. After a
10 residence time of 5 hours, the contents of the autoclave were analysed. The initial rate of carbonylation was only 20 mol CO/grams atom palladium/hour.

Comparative Example D

15 This comparative experiment was carried out in virtually the same manner as the experiment under comparative example C, except that instead of 0.6 mmol 1,4-P,P'bis(diphenylphosphine)butane, 0.6 mmol 1,2-P,P'bis(diphenylphosphine)ethane was used. The reaction rate was less than 20 mol CO /grams atom
20 Palladium/hour.

Comparative Example E

25 This comparative experiment was carried out in virtually the same manner as the experiment under comparative example D, except that instead of 0.6 mmol 1,2-P,P'bis(diphenylphosphine)ethane, 1.0 mmol 1,2-P,P'bis(diphenylphosphine)ethane was used. After a residence time of 5 hours, the contents of the autoclave were analysed. The initial rate of carbonylation was 40 mol CO /grams atom palladium/hour. The total
30 selectivity to butadiene carbonylation products was found to be 60%. The butadiene carbonylation products consisted of 80% pentenoates and 20% diesters.

Comparative Example F

35 This comparative experiment was carried out in virtually the same manner as the experiment under

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comparative example E, except that instead of 1.0 mmol
1,2-P,P'-bis(diphenylphosphine)ethane, 0.6 mmol
1,2-P,P'-bis(ditert-butylphosphine)ethane was used. After
a residence time of 5 hours, the contents of the
5 autoclave were analysed. The initial rate of
carbonylation was only 30 mol CO /grams atom
palladium/hour. The total selectivity to butadiene
carbonylation products was found to be 55%. The butadiene
carbonylation products consisted of 90% pentenoates and
10 10% diesters.

In Table I the phosphorus-containing ligands, the
sources of anions and the quantities of methanol,
phosphorus-containing ligand and source of anions are
stated for each example. The autoclave temperatures and
15 the residence times are also stated in Table I.
Furthermore the results of each example are summarized in
Table I. From the results of the examples it can be
concluded that surprisingly the use of the substituted or
non-substituted phosphorus-containing ligands according
20 to the invention renders the catalyst system much more
active than the conventionally used phosphorus-containing
ligands. As illustrated by comparing comparative
examples A-F with examples 1-5, the initial rate of
carbonylation can be more than doubled, while still
obtaining high selectivities. The use of the substituted
25 phosphorus containing ligand of example 4 is especially
advantageous since here a very high initial rate of
carbonylation in combination with a very high selectivity
to carbonylation and a very high ratio of mono- to
30 diesters is obtained.

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TABLE I

| Example | Catalyst system (apart from palladium cations) | mmol | source of anions mmol |
|---------|---|------|--------------------------------|
| | Phosphorus-containing ligand | | |
| 1 | 1,2-P,P'bis(9-phosphabicyclononyl)ethane | 0.6 | 2, 6-dimethoxybenzoic acid 2 |
| 2 | 1,2-P,P'bis(9-phosphabicyclononyl)ethane | 0.6 | 3-pentenoic acid 5 |
| A | 1,2-P,P'bis(dicyclohexylphosphine)ethane | 0.6 | 2, 6-dimethoxybenzoic acid 2 |
| 3 | 1,2-P,P'bis(9-phosphabicyclononyl)ethane | 0.6 | 2, 6-dimethoxybenzoic acid 5 |
| 4 | 1,2-P,P'bis(1,5-dimethyl, 9-phosphabicyclononyl)ethane | 0.6 | 3-pentenoic acid 10 |
| 5 | P,P'bis(9-phosphabicyclononyl)orthoxylene | 0.6 | 2,4,6-trimethylbenzoic acid 10 |
| B | 1,4-P,P'bis(diphenylphosphine)butane | 1.0 | 3-pentenoic acid 10 |
| C | 1,4-P,P'bis(diphenylphosphine)butane | 0.6 | 3-pentenoic acid 10 |
| D | 1,2-P,P'bis(diphenylphosphine)ethane | 0.6 | 3-pentenoic acid 10 |
| E | 1,2-P,P'bis(diphenylphosphine)ethane | 1.0 | 3-pentenoic acid 10 |
| F | 1,2-P,P'bis(ditert-butylphosphine)ethane | 0.6 | 3-pentenoic acid 10 |

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TABLE I (Cont'd)

| Example | Methanol (Ml) | Temperature (°C) | Residence Time (hr) | Initial Rate of Carbonylation (mol CO / gram atom Pd/hr) | Selectivity to carbonylation (%) | Ratio mono-: diesters |
|---------|------------------|---------------------|------------------------|---|--|-----------------------------|
| 1 | 40 | 170 | 10 | 240 | >95 | 13:87 |
| 2 | 40 | 170 | 10 | 400 | 90 | 57:43 |
| A | 40 | 170 | 10 | 60 | <60 | 95:5 |
| 3 | 40 | 170 | 5 | 350 | >95 | 87:13 |
| 4 | 20 | 150 | 5 | 300 | >95 | 92:8 |
| 5 | 20 | 150 | 5 | 100 | 95 | 99:1 |
| B | 20 | 150 | 5 | 70 | 95 | 98:2 |
| C | 20 | 150 | 5 | 20 | - | - |
| D | 20 | 150 | - | <20 | - | - |
| E | 20 | 150 | 5 | 40 | 60 | 80:20 |
| F | 20 | 150 | 5 | 30 | 55 | 90:10 |

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TS 0801 EPC

C L A I M S

1. A process for the carbonylation of conjugated dienes, whereby an conjugated diene is reacted with carbon monoxide and a hydroxyl group containing compound in the presence of a catalyst system including:

5 (a) a source of palladium cations,
(b) a phosphorus-containing ligand

(c) a source of anions,

wherein the phosphorus-

having the general formula I

$$10 \quad x^1 - R - x^2 \quad (I)$$

wherein X^1 and X^2 represent a substituted or non-substituted cyclic group with at least 5 ring atoms, of which one is a phosphorus atom, and R represents a bivalent organic bridging group, connecting both phosphorus atoms, containing from 1 to 4 atoms in the bridge.

2. A process as claimed in claim 1, wherein the conjugated diene is 1,3-butadiene.

3. A process as claimed in claim 1 or 2, wherein the hydroxyl group containing compound is an alkanol with 1 to 6 carbon atoms per molecule or an alkanediol with 2 to 6 carbon atoms per molecule.

4. A process as claimed in any one of claims 1 to 3, wherein component (a) of the catalyst system is palladium(II) acetate.

5. A process as claimed in any one of claims 1 to 4, wherein component (b) of the catalyst system is a phosphorus-containing ligand of formula (I), wherein the bivalent organic bridging group R is connected to both phosphorus atoms by the first and the second or the third

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carbon atom of a substituted or non-substituted ethylene or propylene group.

6. A process as claimed in any one of claims 1 to 5, wherein component (b) of the catalyst system is a phosphorus-containing ligand of formula (I), wherein X^1 and X^2 represent a substituted or non-substituted bicyclic group with at least 5 ring atoms, of which one is a phosphorus atom.

10 7. A process as claimed in claim 6, wherein component (b) of the catalyst system is a phosphorus-containing ligand of formula (I), wherein X^1 and X^2 represent a substituted or non-substituted [3,3,1] or [4,2,1] 9-phosphabicyclononyl group.

15 8. A process as claimed in claim 7, wherein component (b) of the catalyst system is a phosphorus-containing ligand of formula (I), being a substituted or non-substituted:

20 symmetric or asymmetric [3,3,1] or [4,2,1] isomer of 1,3-P,P'-bis(9-phosphabicyclononyl)propane or a mixture thereof

symmetric or asymmetric [3,3,1] or [4,2,1] isomer of 1,2-P,P'-bis(9-phosphabicyclononyl)propane or a mixture thereof

25 symmetric or asymmetric [3,3,1] or [4,2,1] isomer of 1,2-P,P'-bis(9-phosphabicyclononyl)ethane or a mixture thereof or a mixture of the above mentioned compounds.

9. A process as claimed in any one of claims 7 or 8, wherein one or both of the phosphabicyclononyl rings is substituted with one or more alkyl groups having from 1 to 4 carbon atoms.

30 10. A process as claimed in any one of claims 1 to 9, wherein component (c) of catalyst system contains a protonic acid with a pKa value > 1 in aqueous solution at 25 °C or a salt thereof.

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11. A process as claimed in claim 10, wherein the protonic acid is a carboxylic acid.
12. A process as claimed in claim 11, wherein the carboxylic acid is a benzoic acid.
- 5 13. A process as claimed in claim 12, wherein the benzoic acid is 2,6-dimethoxybenzoic acid.
14. A process as claimed in claim 11, wherein the carboxylic acid is a pentenoic acid.
- 10 15. A process as claimed in any one of claims 1 to 14, wherein component (c) of catalyst system contains a palladium salt.
16. A process as claimed in any one of claims 1 to 15, wherein component (c) of catalyst system contains a combination of an acid and a salt.
- 15 17. A process as claimed in any one of claims 1 to 16, wherein 1,3-butadiene or a derivative thereof is converted into an alkyl pentenoate or a derivative thereof.
18. A process as claimed in any one of claims 1 to 17, 20 wherein 1,3-butadiene is converted into methyl pentenoate.
19. A process as claimed in any one of claims 1 to 16, wherein 1,3-butadiene or a derivative thereof is converted into an alkyl adipate or a derivative thereof.
- 25 20. A process as claimed in any one of claims 1 to 19, wherein the residence time is at most 48 hours.
21. A process as claimed in any one of claims 1 to 20, wherein the ratio of moles of conjugated diene per mole of palladium cation ranges from 1×10^1 to 2×10^7 .
- 30 22. A process as claimed in claim 21, wherein the ratio of moles of conjugated diene per mole of palladium cation ranges from 2×10^2 to 2×10^6 .

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23. A process as claimed in claim 22, wherein the ratio of moles of conjugated diene per mole of palladium cation ranges from 3×10^2 to 2×10^5 .

5 24. A process as claimed in any one of claims 1 to 23, wherein the ratio of moles of conjugated diene per mole of hydroxyl group containing compound ranges from 1:1 to 1:6.

10 25. A process as claimed in any one of claims 1 to 24, wherein the ratio of moles of ligands used per mole of palladium cation ranges from 0.5 to 10.

26. A process as claimed in any one of claims 1 to 25, which is carried out in the presence of a solvent.

15 27. A process as claimed in claim 26, wherein the solvent used includes liquid carbonylation product and/or a carbonylation reactant such as the conjugated diene or the hydroxyl group containing compound.

28. A process according to any one of claims 1 to 27, wherein an extra inert solvent is used.

20 29. A process as claimed in any one of claims 1 to 28, carried out in a stripping reactor.

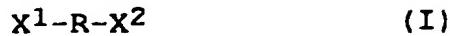
30. A process as claimed in claim 29, wherein a stream of vapour is used to strip carbonylation product from the reactor.

25 31. A process as claimed in claim 30, wherein the stream of vapour comprises at least carbon monoxide.

32. A catalyst system based on:

- (a) a source of palladium cations,
- (b) a phosphorus-containing ligand
- (c) a source of anions,

30 wherein the phosphorus-containing ligand is a ligand having the general formula I



wherein X^1 and X^2 represent a substituted cyclic group with at least 5 ring atoms, of which one is a phosphorus

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atom, and R represents a bivalent organic bridging group, connecting both phosphorus atoms, containing from 1 to 4 atoms in the bridge.

33. A catalyst system as claimed in claim 32, wherein X^1 and X^2 represent a cyclic group with at least 5 ring atoms, of which one is a phosphorus atom, wherein one or both cyclic groups X^1 and X^2 are substituted with one or more hydrocarbyl groups containing carbon atoms and/or hetero atoms.

10 34. A catalyst system as claimed in claim 33, wherein X^1 and X^2 represent a cyclic group with at least 5 ring atoms, of which one is a phosphorus atom, wherein one or both cyclic groups X^1 and X^2 are substituted with one or more alkyl groups having from 1 to 4 carbon atoms.

15 35. A catalyst system as claimed in any of claims 32 to 34, wherein the substituted cyclic group is a substituted bicyclic group with at least 5 ring atoms, of which one is a phosphorus atom.

20 36. A catalyst system as claimed in claim 35, wherein the substituted bicyclic group is a substituted [3,3,1] or [4,2,1] 9-phosphabicyclononyl group.

25 37. A catalyst system as claimed in claim 36, wherein the substituted [3,3,1] or [4,2,1] 9-phosphabicyclononyl group is substituted with two alkyl groups on carbon atom 1, 2 or 8 and carbon atom 4, 5 or 6.

38. A catalyst system as claimed in claim 37, wherein the alkyl groups are methyl groups.

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A B S T R A C T

PROCESS FOR THE CARBONYLATION OF CONJUGATED DIENES

The present invention relates to a process for the carbonylation of conjugated dienes, whereby an conjugated diene is reacted with carbon monoxide and a hydroxyl group containing compound in the presence of a catalyst system including:

- (a) a source of palladium cations,
- (b) a phosphorus-containing ligand
- (c) a source of anions,

wherein the phosphorus-containing ligand is a ligand having the general formula I



wherein X^1 and X^2 represent a substituted or non-substituted cyclic group with at least 5 ring atoms, of which one is a phosphorus atom, and R represents a bivalent organic bridging group, connecting both phosphorus atoms, containing from 1 to 4 atoms in the bridge, whereby the carbonylation process can be performed batch wise, semi-continuously or continuously.

A catalyst system based on:

- (a) a source of palladium cations,
- (b) a phosphorus-containing ligand
- (c) a source of anions,

wherein the phosphorus-containing ligand is a ligand having the general formula I



wherein X^1 and X^2 represent a substituted cyclic group with at least 5 ring atoms, of which one is a phosphorus atom, and R represents a bivalent organic bridging group,

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connecting both phosphorus atoms, containing from 1 to 4 atoms in the bridge.

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